Contact Plating of Organic Thin Films onto a Novel Metal and ITO Plates by Reduction of Nonionic Surfactants Containing an Azobenzene Group

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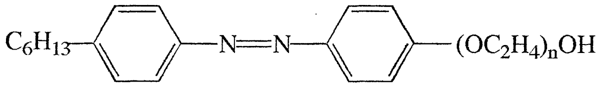
Contact plating of organic thin films is demonstrated onto a noble metal (or ITO) plate short-circuited with an aluminum (or zink) plate in an aqueous dispersion containing organic pigments which are stabilized by nonionic surfactants containing an azobenzene group.

Recently, we demonstrated that micelles formed by redox active surfactants can be dissociated into monomers by electrochemical oxidation or reduction,[1-3] and these phenomena were applied to the electrochemical formation of organic thin films.[4-6] Furthermore, we reported the formation of electroless plating of organic thin films on base metals by simple immersion using nonionic surfactants containing an azobenzene group.[3] However, this method still requires reductive electrolysis for film formation on noble metal and indium tin oxide (ITO) substrates. In this paper, we report contact plating[7] of organic thin films on a noble metal and ITO plates by reduction of the following surfactant:



1: n = 21.4

The preparation of surfactant **1** has been described in our previous paper.[3] As the film-forming materials, β-type copper phthalocyanine (particle size 0.1-0.2 μm, Dainichiseika Color & Chemicals, **2**) and 4,4'-diamino-1,1'-bianthracene-9,9',10,10'-tetrone (0.02-0.04 μm, Ciba-Geigy, **3**) were used. A dispersion containing 1 mM (1 M = 1 mol dm^{-3}) **1**, 0.1 M HCl and 17.5 mM **2** (or 10 mM **3**) was prepared by sonicating the mixture for 10 min and stirring it for three days.

A transparent blue film of **2** was formed on the ITO plate by immersing both the ITO and aluminum (or zink) plates in this dispersion, where these two plates were short-circuited with a metal clip. A blue film was also formed on silver, palladium, gold and platinum plates by the same method. A red film of **3** was also formed by similar method.

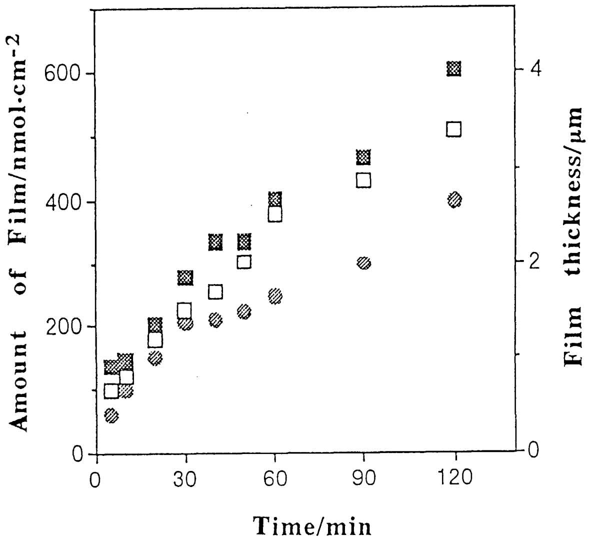


Figure 1. Amount of films of **2** versus immersion time of the substrate in the aqueous dispersion containing 1mM **1**, 17.5 mM **2** and 0.1 M, HCl. Substrate: (▩) ITO, (▨)Ag, (☐), Pt.

Figure 1 shows a plot of the amount of the film of **2** on the ITO plate versus immersion time. After the substrate was covered with the film, this film continued to grow. The film thickness increases with the immersion time and to more than 4 μm. The surfactant seems to be penetrated into the film, owing to the existence of small space in the film.

Absorption spectrum of the film of **2** is very similar to that prepared by vacuum sublimation (Figure 2).[8] Absorption spectrum of an aqueous dispersion prepared by washing these films with an 5 mM Brij 35 aqueous solution consisted of broad peaks and was very similar to that for an 5 mM Brij 35 aqueous dispersion of **2**.[9] The scanning electron micrograph of a cross section of the film of **2** on the ITO plate shows that the film is of uniform thickness (1 μm for 30 min immersion) and is composed of 0.1-0.2 μm particles, which are the same as those used for the dispersion (Figure 3). These agreements indicate that these films are mainly made of **2** and the crystalline form of **2** is maintained throughout the film preparation processes.

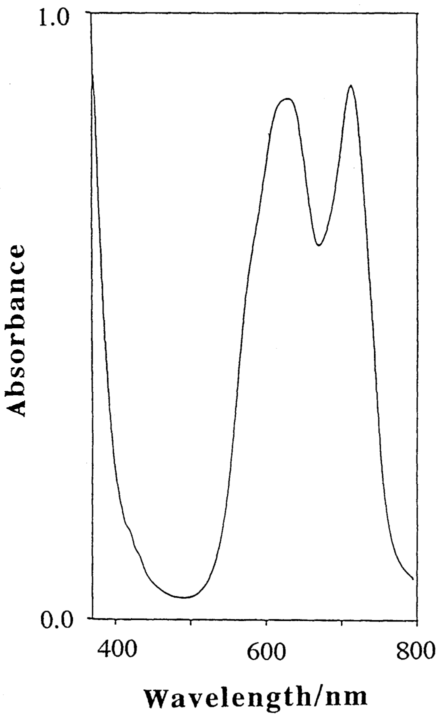


Figure 2. Absorption spectrum of a film of **2** on a ITO prepared by immersing the ITO and aluminum plates in the aqueous dispersion containing 1 mM **1**, 17.5 mM **2** and 0.1 M HCl for 1 min. These two plates were short circuited.

Such film formation on noble metals and ITO may be explained by the same mechanism as that for base metals:[3] **1** is reduced to the aniline derivative at the noble plate short-circuited with an aluminum, which loses its function as a surfactant due to enhancement of the tail group's hydrophilicity. Since the potentials of the plate short-circuited with an aluminum plate in the dispersion (approximately -0.7 V vs. SCE) was more negative than the reduction potential of **1** (approximately -0.1 V[3]).

Present experiments show that the use of **1** makes it possible to prepare a thin film of an organic compound onto a noble metaland ITO plates without electrolysis by applying contact plating technique.

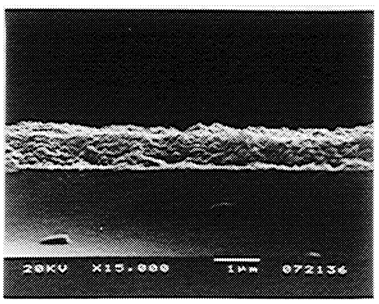


Figure 3. Scanning electron micrograph of a cross section of the film of **2** on the ITO prepared by immersing the ITO and aluminum plates in the aqueous dispersion containing 1 mM **1**, 17.5 mM **2** and 0.1 M HCl for 30 min. These two plates were short-circuited.

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